## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (51) International Patent Classification [7] : <br><br> B01J 23/02, 23/58, 37/02, B01D 53/94 | **A1** | (11) International Publication Number: **WO 00/50168** |
| | | (43) International Publication Date: 31 August 2000 (31.08.00) |

(21) International Application Number: PCT/GB00/00571

(22) International Filing Date: 17 February 2000 (17.02.00)

(30) Priority Data:
9904269.9        24 February 1999 (24.02.99)        GB

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(81) Designated States: CA, JP, NO, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

**Published**
*With international search report.*
*Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: STABILIZATION OF TRANSITION ALUMINA
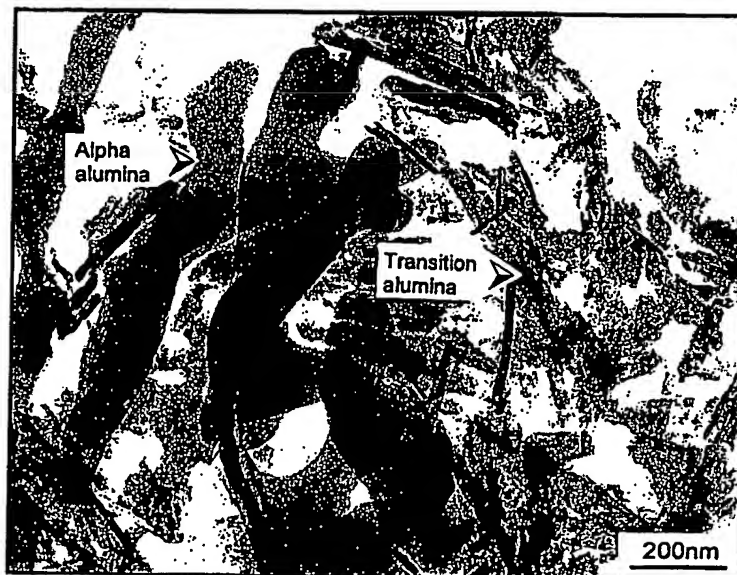
(57) Abstract

The present invention relates to a process for the production of a precursor material for use in the preparation of a stabilized alumina catalyst support material, which process comprises the steps of: (a) providing a mixture comprising aluminium and barium containing compounds; and (b) heating the mixture under conditions to form particles of boehmite at least partially coated with a layer comprising barium and/or a compound of barium.

## Stabilization of Transition Alumina

The present invention relates to the general
field of catalysts, such as automobile exhaust
5    catalysts, and, in particular, to a stabilized
transition alumina catalyst support material.

Rapid developments in combustion technology
coupled with the increasing demands for reduced levels
10   of pollutants emitted by combustion processes has
created a demand for new catalyst materials.  In
particular, new catalysts are needed for temperatures
above 1000°C, not only for the removal of pollutants,
for example to clean up automobile exhausts, but also
15   for catalytic combustion, for example in heaters,
boilers, and gas turbines.  The catalytic combustion
of fuels offers the advantages of a more uniform
combustion temperature and a more complete combustion
of the fuel.  The result is a higher thermal
20   efficiency, together with less nitrogen oxide
formation through the prevention of localised high
temperature areas.

Automobile exhaust catalysts are used to reduce
25   automobile exhaust emissions by converting CO,
unburned hydrocarbons and $NO_x$ in the exhaust gas to an
environmentally less harmful mixture comprising $CO_2$,
$H_2O$ and $N_2$.  The catalysts typically comprise a metal
or ceramic monolithic carrier, such as Cordierite
30   $(2MgO.2Al_2O_3.5SiO_2)$, coated with a high surface area
catalyst support material. Catalytically active noble
metal particles such as, for example, Pt, Pd and/or
Rh, and other additives, are dispersed on and within
the support material.
35

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The catalytically active particles need to be
held in the exhaust gas stream on a support material
which has a high specific surface area to maximize
their exposure to the gas stream and thereby maximize
5       the catalytic efficiency. Gamma-alumina and the
closely related transition aluminas theta and delta
are commonly used as support materials because of
their high specific surface areas. In particular,
gamma-alumina is unusual among ceramic materials in
10      that it has a very high specific surface area, for
example exceeding 100 $m^2/g$, compared with the more
typical values of from about 1 to 5 $m^2/g$ for other
ceramic materials. However, gamma and the other
transition aluminas are metastable phases, which are
15      subject to thermal degradation and undergo a phase
transition at temperatures exceeding about 1000°C to
the thermodynamically more stable alpha-alumina (see
Figures 1 and 9B) with the corollary of a significant
reduction in the specific surface area; typically from
20      about 100 $m^2/g$ to about 1 to 2 $m^2/g$. This results in a
corresponding reduction in catalytic activity. The
transformation sequence for boehmite is gamma → delta
→ theta → alpha. Gamma, delta and theta alumina all
have a cubic oxygen sub-lattice and the only
25      difference between them is in the progressive increase
in ordering of aluminium atoms on the cation deficient
aluminium sub-lattice. In contrast, alpha-alumina has
a hexagonal oxygen sub-lattice and its formation
involves a total restructuring of the lattice.
30

Thermal degradation of transition alumina is a
kinetic effect which accelerates rapidly with
increasing temperature. Whereas at 600°C it is too
slow to be significant within the lifetime of a
35      catalytic converter, at 1100°C it may be complete

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within 1 hour.  Catalytic converters are operated at
the upper limit of their stability and catalyst
support materials with improved resistance to thermal
degradation would allow higher operating temperatures
5    and a longer service life.

Automotive exhaust gases from petrol engines may
contain up to 3% CO and 100 ppm unburned hydrocarbons
which react exothermically in the catalytic converter
10   with $NO_x$ to yield an environmentally less harmful
mixture of gases, namely $CO_2$, $H_2O$ and $N_2$. Peak
operation temperatures of from about 700°C to about
800°C are frequently achieved. The current trend to
reduce $CO_2$ emissions has resulted in increased use of
15   diesel engines with lower fuel consumption and hence
lower $CO_2$ emissions. However, diesel engines operate
at higher exhaust temperatures; approximately 800°C is
normal with peak temperatures of up to about 1300°C.

20       The conventional solution to the thermal
degradation of gamma and the other transition aluminas
is the use additives, such as, for example, Zr, Ba,
Ce, La, Si, either singly or in combination.
US-4,624,940 relates to a catalyst for the oxidation
25   of carbon monoxide and unburned hydrocarbons in an
exhaust stream.  The catalyst comprises support
particles of stabilized gamma-alumina having palladium
dispersed thereon and can remain effective after
exposure to temperatures greater than 1000°C.  The
30   gamma-alumina is stabilized by either (i)
incorporation of a combination of lanthana and baria
into the alumina particles, or (ii) impregnation of
the alumina particles with an aqueous dispersion of a
high molecular weight polyorganosiloxane followed by
35   heating to a temperature which is effective to

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decompose the polyorganosiloxane. The additives are
introduced by soaking an alumina powder or a solid
alumina precursor in a solution containing the
additive followed by drying and calcining at a
5    temperature sufficient to effect stabilization.  An
alternative but ·less widely used method of introducing
additives is by a coprecipitation process as described
in US-4,056,489.  In this manner an intimate admixture
of alumina and the stabilizing additives is formed,
10   which is then calcined.


The present inventors have now devised a process
whereby transition alumina can be further stabilized
against thermal degradation to alpha-alumina.  This
15   results in a catalyst which is effective at higher
operating temperatures and for longer times compared
with the prior art catalysts.


Accordingly, in a first aspect the present
20   invention provides a process for the production of a
precursor material for use in the preparation of a
stabilized alumina catalyst support material, which
process comprises the steps of:

25   (a)   providing a mixture comprising an aluminium
containing compound and at least one additive
selected from barium, zirconium, cerium,
lanthanum, calcium and silicon containing
compounds; and

30

(b)   heating the mixture under conditions to form
particles of boehmite at least partially coated
with a layer comprising at least one of barium,
zirconium, cerium, lanthanum, calcium and silicon
35       and/or at least one compound containing barium,

zirconium, cerium, lanthanum, calcium and/or silicon.

Boehmite is a mineral form of aluminium monohydroxide (AlO.OH).

The additive is preferably a barium containing compound. The layer formed on the particles of boehmite preferably comprises barium carbonate.

An important advantage of the process according to the present invention is that the particles of boehmite can be substantially coated completely with the said layer.

The mixture in step (a) is preferably a substantially homogenous mixture. The substantially homogenous mixture may be formed by any process which results in an intimate admixture. For example, by forming a slurry of boehmite and/or gamma alumina with a water-soluble compound of barium, such as barium nitrate, or, alternatively, by adding a barium containing solution to a gel comprising an aluminium containing compound.

A particularly preferred process for forming the substantially homogenous mixture is by homogeneous precipitation, ideally homogeneous precipitation of water-soluble aluminium and barium containing compounds, for example salts thereof. Suitable aluminum compounds include aluminium nitrate, aluminium sulphate and/or aluminium chloride, preferably aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$). Suitable barium compounds include barium nitrate, barium sulphate and/or barium chloride, preferably barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$).

Precipitation from aqueous solution is widely used for producing ceramic oxide powders. Precipitation occurs by adding a precipitating ligand

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(anion) to a solution containing cations of the
appropriate metal. If the precipitating ligand is
added directly by simply pouring one solution into
another then there is little control of the chemistry
5      during precipitation because of the large and
inhomogeneous gradients in solution concentration.
Better control of chemical and morphological
characteristics can be achieved if the precipitating
ligands are generated "in situ", simultaneously and
10     uniformly throughout the solution. This is know as a
"homogeneous" precipitation process. In a preferred
aspect of the present invention the mixture in step
(a) is formed by homogeneous precipitation in which a
base is generated within a metal salt solution through
15     thermal decomposition of a suitable water-soluble
reagent. Suitable water-soluble reagents include any
compound that decomposes on heating in aqueous
solution to release $NH_3$ groups, thereby forming
ammonium hydroxide which increases the pH of the
20     solution. Examples include urea and amines, such as
hexamethylene tetramine. Suitable compounds of
aluminium include aluminium nitrate, aluminium
sulphate and/or aluminium chloride, preferably
aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$). Suitable
25     compounds of barium include barium nitrate, barium
sulphate and/or barium chloride, preferably barium
chloride dihydrate ($BaCl_2 \cdot 2H_2O$). A small amount of a
dispersant, for example polyvinylpyrrolidone, may also
be added to the metal salt solution. The dispersant
30     improves the uniformity of the precipitation product
by reducing the tendency of the precipitate particles
to stick together. Additionally, diffusion of ionic
species through an adsorbed dispersant-layer may be
the rate limiting step to further particle growth.
35

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The mixture comprising aluminium and barium
containing compounds will generally be in the form of
a gel when produced by the homogeneous precipitation
process described above, although the mixture can take
5     other forms including, for example, hydroxides,
molecular and ionic complex species or compounds. The
gel is a three-dimensional network of colloidal
particles of mainly amorphous aluminium hydroxide
containing a large amount of water (for example
10   approximately 170 g of wet gel yields approximately 7
g of dried powder) and in which the barium additive is
trapped. The consistency of the gel is generally
between that of a thick paste and a jelly, and it
easily breaks up when stirred in an excess of water
15   and slowly settles to the bottom again.

The mixture comprising aluminum and barium
containing compounds may also be formed by adding a
water-soluble barium compound, for example barium
20   nitrate, barium sulphate and/or barium chloride, to a
slurry of, for example, boehmite in water.
Advantageously, an organic acid, such as a carboxylic
acid is added to the mixture. A preferred carboxylic
acid is oxalic acid. In a particularly preferred
25   aspect, a solution comprising barium nitrate and
oxalic acid is added to the slurry of boehmite in
water and the mixture is then heated under conditions
to produce particles of boehmite at least partially
coated with a layer comprising barium and/or a barium
30   compound.

The heating in step (b) is preferably achieved by
a hydrothermal treatment, which is typically carried
out on an aqueous solution of the mixture of aluminium
35   and barium containing compounds in a pressure vessel,

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such as an autoclave, at a temperature above the
normal boiling point and under applied or autogenous
pressure to substantially prevent boiling. The
hydrothermal treatment will generally be performed at
5    a temperature typically in the range of from 90 to
300°C, more typically from 100 to 220°C. It will be
appreciated that the pressure required to
substantially prevent boiling will depend on the
applied temperature. Typically, the hydrothermal
10   treatment is performed at a pressure in the range of
from 1 to 150 bar, more typically from 5 to 50 bar,
still more typically from 10 to 40 bar. The
hydrothermal treatment is typically carried out for a
time in the range of from 30 minutes to 25 hours, more
15   typically from 1 to 10 hours.

        The heating in step (b) may also be achieved by
heating at a temperature in the range of from ambient
temperature to boiling temperature. This may readily
20   be achieved by a reflux operation, which may be
carried out, for example, at atmospheric pressure and
a temperature in the range of from 80 to 120°C,
preferably approximately 100°C.

25       In one aspect of the present invention, the
process of forming coated boehmite particles from a
solution comprising aluminium and barium containing
compounds can be seen to involve sequential
precipitation: first, the formation of an aluminium
30   hydroxide gel; second the precipitation of barium
and/or a barium compound (probably as a carbonate)
within the gel at a higher pH to give a uniform
mixture; third crystallization of boehmite particles;
and fourth precipitation or re-precipitation of barium
35   and/or a barium compound (probably as a carbonate) on

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the surface of the boehmite particles.

The product of the process according to the first aspect of the present invention may subsequently be dried and then calcined. Drying and calcination will generally be carried out in air or other oxidizing atmosphere.

In a second aspect, the present invention provides a process for the preparation of a stabilized alumina catalyst support material, which process comprises the steps of:

(i) providing a precursor material comprising particles of boehmite at least partially coated with a layer comprising barium and/or a compound of barium; and

(ii) heating the coated particles of boehmite to a temperature at which at least some of the boehmite transforms to gamma-alumina.

In the second aspect, heating is typically carried out at a temperature in the range of from 500 to 1000°C. The process may also include an additional step of further heating whereby at least some of the gamma-alumina transforms to theta and/or delta-alumina. The further heating is typically carried out at a temperature in the range of from 1000 to 1400°C. Heating will generally be carried out in air or other oxidizing atmosphere.

The precursor material comprising particles of boehmite may be unsupported or may be provided in the form of a washcoat on a catalyst carrier substrate,

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such as a ceramic honeycomb.

The gamma-alumina particles produced according to the second aspect of the present invention may be provided in the form of a dry powder which can be redispersed in an appropriate liquid, such as water, to form a slurry or washcoat.

The precursor material may be produced according to a process as herein described with reference to the first aspect of the invention.

In a third aspect, the present invention provides a process for the preparation of a catalyst, such as an automotive catalytic converter, which process comprises the steps of dispersing a precursor mixture comprising particles of boehmite at least partially coated with a layer comprising barium and/or a compound of barium on a metal or ceramic monolithic substrate, followed by heating the precursor mixture to a temperature at which at least some of the boehmite transforms to gamma-alumina.

In the third aspect, heating is typically carried out at a temperature in the range of from 500 to 1000°C. The process may also include an additional step of further heating whereby at least some of the gamma-alumina transforms to delta and/or theta-alumina. The further heating is typically carried out at a temperature in the range of from 1000 to 1400°C. Again, heating will generally be carried out in air or other oxidizing atmosphere.

The mixture can be dispersed on to metal or ceramic monolithic substrate in a conventional manner,

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for example by dipping the substrate one or more times
into an aqueous slurry (washcoat) of the coated
boehmite powder, followed by drying.

5          In the second and third aspects of the present
invention, the particles of gamma-alumina, theta,
delta-alumina and/or boehmite will typically be at
least partially coated with a layer comprising barium
and/or a compound of barium. The layer will typically
10    comprise one- or more of barium carbonate, barium oxide
and/or barium aluminate depending on the heat-
treatment. For gamma-alumina particles, the layer
will generally comprise barium oxide as the major
constituent, whilst for theta and delta-alumina
15    particles, the layer will generally comprise one or
more barium aluminates as the major constituent(s).

          In a fourth aspect, the present invention
provides a process for the preparation of a catalyst,
20    such as an automotive catalytic converter, which
process comprises the step of dispersing a stabilized
alumina catalyst support material as herein described
on a metal or ceramic monolithic substrate.

25          Again, the stabilized alumina catalyst support
material may be dispersed on to the metal or ceramic
monolithic substrate in a conventional manner, for
example by dipping the substrate one or more times
into an aqueous slurry (washcoat) of stabilized
30    alumina powder, followed by drying.

          In a fifth aspect, the present invention provides
a precursor material for use in the preparation of
catalyst support material, which precursor material
35    comprises particles of boehmite and/or transition

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alumina at least partially coated with a layer comprising barium and/or a compound of barium.

Each particle of boehmite and/or transition alumina preferably has a substantially uniform surface layer comprising barium and/or a compound of barium. The layer will typically comprise one or more of barium carbonate, barium oxide and/or barium aluminate depending on the heat-treatment used to process the particles. For boehmite, the layer will generally comprise barium carbonate as the major constituent; for gamma-alumina particles, the layer will generally comprise barium oxide as the major constituent; and for theta and delta-alumina particles, the layer will generally comprise one or more barium aluminates as the major constituent(s).

The size of the particles may range from 10 nm to 5 μm, but the particles typically have an average particle size in the range of from 100 to 500 nm. In general the particles take the form of thin prismatic crystals with an average length to width ratio typically of about 3:1. The average length to thickness ratio is typically in the range of from 10:1 to 20:1. The crystal sizes are for the longest dimension. The surface layer comprising barium and/or a compound of barium will typically be up to 5 nm in thickness, more typically up to 3 nm in thickness.

The precursor material may provided in the form of an aqueous slurry, a non-aqueous slurry or a powder.

In a sixth aspect, the present invention provides a stabilized alumina catalyst support material which

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comprises gamma, theta and/or delta-alumina, and which
withstands substantial degradation to alpha-alumina
after exposure to a temperature of approximately
1400°C for 1 hour when heated in, for example, air or
5    other oxidizing atmosphere.

In this aspect, the stabilized alumina catalyst
support material preferably has a specific surface
area of at least 20 $m^2/g$, more preferably at least
10   25 $m^2/g$, still more preferably at least 31 $m^2/g$, after
exposure to a temperature of 1400°C for 1 hour. The
specific surface area is measured using the standard
BET method.

15   In a seventh aspect, the present invention
provides a catalyst, such as an automotive catalytic
converter, which comprises a metal or ceramic
monolithic substrate having dispersed thereon a
stabilized alumina catalyst support material as herein
20   described.

It will be appreciated that one or more
catalytically active noble metal particles, for
example Pt, Pd and/or Rh, optionally together with
25   other additives, will typically be dispersed on the
support material.

In the third, fourth and seventh aspects the
catalyst may be a 3-way automotive catalytic
30   converter.

The monolithic substrate can be formed from any
of the conventional ceramic materials in the art
including, for example, one or more of cordierite,
35   cordierite-alpha alumina, silicon nitride, silicon

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carbide, mullite, zirconia-mullite, spodumene, alumina-silica-magnesia and/or zirconium silicate. Examples of suitable metal substrates include austenitic stainless steel and high aluminium ferritic
5    stainless steel.

It will be appreciated that the stabilized alumina according to the present invention may be used in conjunction with other components conventionally
10   used in the field of catalysis, such as, for example: catalytic promoters, including Ni, Co, Mn, $Cr_2O_3$, $TiO_2$, $ZrO_2$ and/or $CeO_2$; washcoat stabilization oxides, including cordierite, mullite and/or magnesium aluminium titanate; additional stabilization
15   additives, including Zr, Ce, La, Ca, Cu, Th and/or Si.

The present invention will now be described further, by way of example, with reference to the following drawings, in which:
20

Figure 1 is a TEM micrograph of alumina without additive showing the transformation of transition-alumina to alpha-alumina with a reduction in specific surface area;
25

Figure 2 is a TEM micrograph of a hydrothermally treated material showing large alpha-alumina crystals and nanoparticles of barium aluminate. The material was formed by heating a
30   hydrothermally treated alumina-baria precursor to 1400°C for 1 hour in argon;

Figure 3 is a TEM micrograph showing a porous boehmite crystal pseudomorph consisting of gamma-
35   alumina coated with a barium oxide layer. The

material was formed by heating a hydrothermally-
treated precipitate of an alumina-baria precursor
to 1000°C for 1 hour;

5    Figures 4 shows TEM micrographs of boehmite
pseudomorphs consisting of theta-alumina
particles exhibiting a twinned structure and some
residual porosity.. The material was formed by
heating a hydrothermally-treated precipitate of
10    alumina-baria precursor to 1400°C for 1 hour;

Figure 5 A and B are TEM micrographs showing a
comparison between boehmite produced by a
hydrothermal treatment of a precipitate of an
15    alumina-baria precursor and theta-alumina formed
by heating the same boehmite: (A) boehmite
produced by a hydrothermal treatment of a
precipitate of an alumina-baria precursor, and
(B) theta-alumina formed by heating the boehmite
20    to 1400°C for 1 hour;

Figure 6 is a flow chart showing a synthesis
procedure for making alumina-baria precursor
gels;

25

Figure 7 is a DTA analysis of an autoclave
treated alumina-baria precursor gel for various
heating rates.

30    Figures 8 A-D are TEM micrographs of an oven-
dried alumina-baria precursor gel: (A) and (B)
microcrystalline bayerite before calcination,
bright and dark filed respectively, (C) and (D)
gamma-alumina with crystals of $\beta_{II}$ after 1 hour at
35    1000°C, bright and dark field respectively;

Figures 9 A-F are TEM micrographs of a microwave
treated alumina-baria precursor gel: (A)
morphology after microwave drying, (B) large
alpha-alumina crystal growing in matrix of theta-
alumina after 1 hour at 1200°C in air, (C) and
(D) nano-particles of $\beta_I$ inside alpha-alumina
crystals after 1 hour at 1400°C in air, (E) and
(F) nano-particles of $\beta_I$ inside and on the
surface of alpha-alumina crystals after 1 hour at
1400°C in argon;

Figure 10 A-C are TEM micrographs of an autoclave
treated alumina-baria precursor gel: (A) well-
developed boehmite crystals after hydrothermal
treatment of 4 hours at 210°C, (B) porous
boehmite pseudomorphs after 1 hour at 1000°C, and
(C) detail showing size, shape and orientation of
pores;

Figures 11 A-D are TEM micrographs of an
autoclave treated alumina-baria precursor gel
after calcination for 1 hour at 1400°C in air:
(A) boehmite pseudomorphs comprising theta-
alumina, (B) finely twinned theta-alumina with
equiaxed pores, (C) and (D) details of twinned
theta-alumina structure showing twin lamella as
narrow as 5 nm; and

Figures 12 A and B are TEM micrographs of an
autoclave treated alumina-baria precursor gel
after calcination for 1 hour at 1400°C in argon:
(A) nano-particles of $BaAl_{12}O_{19}$ in a matrix of
theta-alumina transformed extensively to alpha-
alumina, (B) detail showing $BaAl_{12}O_{19}$ particles
predominantly on the surface of the alpha-

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alumina.

The present inventors have investigated a number
of ways of introducing barium additives to gamma-
alumina and have found that they all yield similar
results to those already known except for two methods
which yielded a product with a markedly superior
resistance to thermal degradation.  The process
according to the present invention relies on a
hydrothermal or refluxing treatment of a substantially
homogeneous mixture of aluminium and barium containing
compounds.

The hydrothermal or refluxing treatment results
in crystals of boehmite which appear to be coated with
a layer of barium or a barium compound some nanometres
thick.  The layer is thought to be barium carbonate.
Boehmite (AlO.OH) is an aluminium monohydroxide which
is a gamma-alumina precursor.  On heating to about
500°C, boehmite transforms to gamma-alumina without a
substantial change in external crystal shape, but with
the development of internal porosity, which is thought
to be responsible for the unusually high specific
surface area of gamma-alumina.  It seems that by
depositing the barium as a substantially uniform
surface coating, the effectiveness of the barium as a
stabilizer for gamma-alumina is maximized and that the
hydrothermal or refluxing method is therefore markedly
superior to other methods such as calcining that yield
a more or less homogeneous mixture of phases.

On heating, the hydrothermally treated material
transforms to gamma-alumina at temperatures up to
about 1000°C (see Figure 3) and transition alumina
(theta and delta phases) at temperatures up to about

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1400°C for about 1 hour (see Figure 4). The layer
comprising the barium-containing compound, possibly
barium carbonate, transforms first to barium oxide on
heating to about 830°C in the pure state and then
5   subsequently to barium aluminate.

After heating to a higher temperature, X-ray
diffraction showed that the barium formed barium oxide
at temperatures up to about 1000°C and various barium
10  aluminates (for example $BaAl_2O_4$, $BaAl_{13.2}O_{20.8}$ and
$BaAl_{9.2}O_{14.8}$) at higher temperatures. These phases were
present in all samples, not just in the case of the
hydrothermally treated samples.

15  Barium aluminates are believed to be effective in
preventing the nucleation of alpha-alumina if a
sufficient quantity is present on the surface of
gamma-alumina particles to fill surface defects which
otherwise act as nucleation sites for the phase
20  transformation to alpha-alumina.

In microwave-treated materials after about 1 hour
at approximately 1200°C, barium aluminate ($BaAl_{13.2}O_{20.8}$)
was visible as nano-sized particles predominantly
25  inside much larger alpha-alumina crystals in
transmission electron micrographs and was particularly
well-developed after about 1 hour at approximately
1400°C (see Figures 9C and 9D), whereas in
hydrothermally-treated alumina such particles were
30  absent after treatment at 1400°C, except when heated
in argon instead of air, in which case nano-sized
particles of barium aluminate ($BaAl_{12}O_{19}$) were visible,
predominantly on the surface of the alpha-alumina
crystals (see Figure 2). The conclusion is that
35  barium aluminate was present as a thin surface layer

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in the hydrothermally treated material even after 1 hour at 1400°C in air, but not in a similar starting material treated by oven-drying or microwave-drying because those materials transformed or partly transformed to alpha-alumina after 1 hour at 1200°C, a temperature similar to that reported by other authors. An important step therefore seems to be the formation of a generally uniform surface layer of barium and/or a barium compound on the boehmite crystals during the hydrothermal or refluxing treatment.

The length of hydrothermal treatment is important in determining the specific surface area of the product after the subsequent high temperature treatment. After heating for 1 hour at 1400°C, a material that was previously given a 4 hour hydrothermal treatment at approximately 210°C resulted in theta-alumina with a specific surface area of 6 m²/g. In contrast, after heating for 1 hour at 1400°C, a material that was previously given a 22 hour hydrothermal treatment at 210°C resulted in theta-alumina with a more useful specific surface area of 31 m²/g. Such a material would retain sufficient surface area to remain effective as a catalyst support material. Figures 5A and 5B shows that there is remarkably little change in general appearance of the hydrothermally treated material before (5A) and after (5B) heating for 1 hour at 1400°C which demonstrates the effectiveness of this material in resisting thermal degradation.

The present invention will now be described further with reference to the following Examples and Comparative Examples.

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## Examples

Aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$)
(Merck, crystalline, purified), barium chloride
5   dihydrate ($BaCl_2 \cdot 2H_2O$) (Baker, analysed, reagent
grade), urea ($CON_2H_4$) (Acros, p.a.) and
polyvinylpyrrolidone (PVP, Aldrich, K-30, special
grade) were used as received. Solutions of the above
reagents were filtered before use.
10

Alumina and alumina doped with approximately 10
mol% baria were synthesised by homogeneous
precipitation from a metal salt solution induced by
the thermal decomposition of urea as shown in the flow
15   chart in Figure 6. On heating the solution to
approximately 86°C, the urea decomposed to produce a
controlled and uniform increase in pH until
precipitation occurred. Very fine sol particles
sedimented from the solution after standing for
20   several hours at room temperature. The reaction
product was centrifuged to separate the
characteristically voluminous and transparent gel.
The gel was washed twice with double its own volume of
distilled water to remove most of the anion and
25   organic impurities. About 1200 ml of the transparent
gel was produced from 5 l of solution in a typical
experiment.

Some $Ba^{2+}$ was detected qualitatively in the
30   washing water by precipitation with $SO_4^{2-}$. The loss of
barium could be avoided by omitting the washing step,
in which case the chloride anion was removed by
sublimation of $NH_4Cl$, either during microwave drying,
or during calcination in the case of the oven-dried
35   specimens. For autoclave treated gels, washing

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carried out after crystallisation of boehmite and barium carbonate removed chloride ions without a loss of barium.

5          The alumina and alumina-baria gels were treated in a variety of different ways:  air-dried at room temperature;  oven-dried at a temperature in the range of from 90 to 100°C;  dried in a microwave oven;  and hydrothermally treated in an autoclave.  The air-dried

10     gel was prepared by leaving the gel in a glass beaker at room temperature until a solid formed which was then crushed in an agate mortar to produce a fine powder.  The oven-dried gel was prepared by heating the gel in air in an oven at about 90 to 100°C for

15     approximately 24 hours;  the solid was then crushed as above to produce a fine powder.  The microwave-dried samples of gel were prepared in a standard domestic microwave oven at a power setting of 500 W using cycles of 5 min power on and from 2 to 3 min power

20     off, because of extensive foaming of the gel due to the release of gaseous products.  The dried solid was crushed as above and later calcined at different temperatures.  The hydrothermal treatment was conducted on 150 ml samples of centrifuged gel in 230

25     ml Teflon-lined pressure-tight steel containers.  A heating rate of about 0.5°C/min to a temperature of 210 ± 5°C was used.  The hold time at the temperature was about 4 hours.  The resulting brownish liquor with a pH in the range of from 8 to 8.5 was decanted and

30     the crystallised product was dried at a temperature from 90 to 100°C.  The crystalline product was calcined in either air or argon.

          The size of the colloidal particles in the
35     alumina and alumina-baria gels was measured by Small

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Angle X-ray Scattering (SAXS); evaluation of the
results of this technique was based on the assumption
that the gel was a fractal system (see J. Teixeira, J.
Appl. Cryst. 21 (1988) 781). The phase composition of
5      the samples was determined by XRD, either in-situ
during calcination (Siemens D5000), or conventionally
before and after calcination at various temperatures
(Philips PW173). Thermal decomposition of the gel to
the calcined products on heating to 1400°C was
10     observed by differential thermal analysis and
thermogravimetry (DTA/TG, Netsch Simultaneous Analyser
STA 409). Transmission electron microscopy (TEM,
Philips EM 400) and High Resolution Transmission
Electron Microscopy (HRTEM, JEOL 4000 EX/II with a
15     point resolution of 0.165 nm at 400 kV) were used for
analysis of the fine structure of uncalcined and
calcined samples. Electron microscopy samples were
prepared by dispersing the powder in ethyl alcohol,
placing a drop of this suspension on a carbon-coated
20     copper grid, and allowing the alcohol to evaporate.
The specific surface area was measured by BET nitrogen
adsorption (Coulter-Omnisorp 360).

The important characteristic of the homogeneous
25     precipitation process was that it yielded a product
substantially uniform both in chemical composition and
particle size. The decomposition of urea on heating
the solution released ammonium ions into solution in a
very uniform manner resulting in a gradual and uniform
30     increase in pH. These uniform conditions ensured that
the alumina-baria composite gel which precipitated
from the dissolved chloride salts was substantially
chemically homogeneous on a colloidal scale. The
precipitation kinetics were easily controlled through
35     the heating rate and the ageing temperature. The flow

- 23 -

chart in Figure 6 summarises the steps and conditions of the synthesis.

5    The size of the sol particles in the gel samples was calculated from SAXS measurements as shown in Table 1. The alumina and alumina-baria precursor gels both consisted of particles of about 4 nm diameter and the fractal dimension indicates that both gels were in a similar state of aggregation.

10

|                      | Alumina | Alumina-baria |
|----------------------|---------|---------------|
| Fractal dimension    | 2.2     | 2.4           |
| Particle diameter (nm) | 3.7   | 4.1           |

15

Table 1: Properties of alumina and alumina-baria precursor gel measured by SAXS

20    The phase evolution during calcination was studied by X-ray diffraction "in-situ" and conventionally, i.e. on specimens measured at room temperature after calcination. The main results for the conventional measurements are summarised in

25    Table 2 with phases listed in order of abundance. The phases in alumina-baria samples were compared with those in pure alumina samples to obtain information on the effects of each of the gel treatment techniques.

30

| Sample | Phases determined by XRD | | | | |
|---|---|---|---|---|---|
| | air | | | | argon |
| | uncalcined | 1000°C 1h | 1200°C 1h | 1400°C 1h | 1400°C 1h |
| oven dried 100°C 24h | amorphous bayerite urea (tr) | $\gamma$-Al$_2$O$_3$ BaO | $\alpha$-Al$_2$O$_3$ BaAl$_2$O$_4$ $\beta_I$ | $\alpha$-Al$_2$O$_3$ $\beta_I$ | nd |
| microwave dried | amorphous boehmite BaAl$_{12}$O$_{19}$(i) | $\gamma$-Al$_2$O$_3$ $\beta_{II}$(tr) | $\alpha$-Al$_2$O$_3$ $\theta$-Al$_2$O$_3$ $\beta_I$ | $\alpha$-Al$_2$O$_3$ $\beta_I$ | $\alpha$-Al$_2$O$_3$ $\beta_I$ |
| autoclaved 4h | boehmite BaCO3(i) | $\gamma$-Al$_2$O$_3$ $\delta$-Al2O3 BaO(i) | $\theta$-Al$_2$O$_3$ $\delta$-Al$_2$O$_3$ BaAl$_2$O$_4$ | $\theta$-Al$_2$O$_3$ $\delta$-Al$_2$O$_3$ BaAl$_2$O$_4$ $\beta_{II}$ | $\alpha$-Al$_2$O$_3$ $\theta$-Al$_2$O$_3$ BaAl$_{12}$O$_{19}$ |
| autoclaved 22h | nd | nd | nd | $\theta$-Al$_2$O$_3$ BaAl$_2$O$_4$ $\beta_{II}$ | nd |

$\beta_I = $ BaAl$_{13.2}$O$_{20.8}$, (BaO·6.6Al$_2$O$_3$), $\beta_{II} = $ BaAl$_{9.2}$O$_{14.8}$, (BaO·4.6Al$_2$O$_3$), tr = traces, (i) only most intense peaks visible, nd = not determined

**Table 2: Phase composition of alumina-baria samples before and after calcination of dehydrated gel.**

The alumina-baria gel dried at room temperature appeared to be amorphous from the XRD spectra. The only indication of the presence of a crystalline phase was a small amount of retained urea. The XRD spectrum for the oven-dried sample (100°C) also indicated predominantly amorphous material and the presence of very poorly crystallized bayerite Al(OH)$_3$, besides traces of crystalline urea. There was no indication of the presence of any crystalline barium containing

phase.

In the microwave-treated alumina sample, "in situ" XRD indicated the presence of microcrystalline
5      boehmite to approximately 400°C at which temperature the sample became amorphous and remained amorphous to about 800-850°C when transition alumina ($\gamma$-Al$_2$O$_3$) appeared. At about 950-1000°C transformation of $\gamma$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$ began and was almost complete at
10     1200°C. In the microwave-treated alumina-baria sample, the phase initially present was also microcrystalline boehmite (or pseudo boehmite) which became amorphous at about 400°C. The transition aluminas that formed were $\gamma$-Al$_2$O$_3$ and $\theta$-Al$_2$O$_3$ instead
15     of just $\gamma$-Al$_2$O$_3$ as in the pure alumina sample. The transformation from $\theta$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$ began at about 1050-1100°C. After calcination at 1000°C for 1 hour traces of the BaAl$_{9.2}$O$_{14.8}$ ($\beta_{II}$) phase were present. After calcination for 1 hour at 1200°C or 1400°C,
20     BaAl$_{13.2}$O$_{20.8}$ ($\beta_I$) was present instead of $\beta_{II}$. Calcination in argon or argon and air for 1 hour at 1400°C gave the same result.

In the autoclave treated alumina and alumina -
25     baria precursor gels XRD showed that the samples initially consisted of well-crystallised boehmite which decomposed at 450-500°C to an amorphous phase. Two rather weak peaks corresponding to the main peaks in the spectrum for $\gamma$-barium carbonate were also
30     detected. In-situ XRD showed that the two BaCO$_3$ peaks persisted to 700°C at which temperature a peak corresponding to the main BaO peak appeared and transition alumina formed. After 1 hour at 1000°C, $\gamma$-Al$_2$O$_3$, $\delta$-Al$_2$O$_3$ and BaO were the phases present. After
35     1 hour at 1200°C $\gamma$-Al$_2$O$_3$, $\delta$-Al$_2$O$_3$ and BaAl$_2$O$_4$ were

present. After 1 hour at 1400°C, $\theta$-$Al_2O_3$ and $\delta$-$Al_2O_3$ were present with $BaAl_2O_4$ and $BaAl_{9.2}O_{14.8}$ ($\beta_{11}$). A trace amount of $\alpha$-$Al_2O_3$ was found in this sample calcined in air for 1 hour and, after 10 hours at 1400°C, $\theta$-$Al_2O_3$ was still the predominant phase. However, in samples calcined in argon for 1 hour at 1400°C the principle phase was $\alpha$-$Al_2O_3$.

The DTA/TG curves in Figure 7 for the hydrothermally treated baria-doped samples show well-defined exothermic peaks corresponding to the decomposition of boehmite by dehydroxylation. A displacement of the dehydroxylation peaks to higher temperatures with increased heating rate indicates the slow kinetics of dehydration. The theoretical weight loss for the dehydroxylation of boehmite is 15%. In Ba doped boehmite a weight loss of less than 15% was expected whatever barium compound was present, for example carbonate or hydroxide, due to the high atomic weight of barium compared with aluminium. There was no indication of Ba phases such as $BaCO_3$ or $Ba(OH)_2 \cdot xH_2O$ which have a number of well-defined peaks by which they could easily be identified if present.

BET surface area measurements were made on samples calcined for 1 hour at either 1200°C or 1400°C. For calcination at 1200°C, a value of 45.2 $m^2/g$ was measured for specimens autoclaved for 4 hours. For calcination at 1400°C, values of 5.9 $m^2/g$ and 31.2 $m^2/g$ were obtained for specimens autoclaved for 4 hours and 22 hours respectively. The longer autoclave treatment resulted in larger boehmite crystal size in the sample before calcination. After calcination at 1400°C, the phase composition of the specimens was also different. From XRD analysis, the

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phases present in order of abundance in the specimen
autoclaved for 4h were: $\theta$-$Al_2O_3$, $\delta$-$Al_2O_3$, $BaAl_2O_4$ and
$\beta_{11}$. The specimen autoclaved for 22 hours differed in
that $\delta$-$Al_2O_3$ was absent.

5

     TEM examination showed that considerable
morphological differences existed between oven-dried,
microwave-dried and hydrothermally treated samples,
both before and after calcination.

10

     Before calcination, the oven-dried material
consisted of densely agglomerated fine crystals,
Figures 8A and 8B, which were identified by electron
diffraction as bayerite. The microwaved material was
15    much less tightly agglomerated as shown in Figure 9A
and consisted of boehmite crystallites of about 5 nm
as seen by HRTEM (not shown here) which approximately
correspond to the size of the colloidal particles in
the gel. The hydrothermally treated sample consisted
20    of plate-like boehmite crystals about 250 x 100 x 10
nm as shown in Figure 10A. There was no evidence of a
separate Ba containing phase in any of the uncalcined
samples.

25    TEM micrographs of oven-dried material calcined
for 1 hour at 1000°C indicated the presence of a $\gamma$-
$Al_2O_3$ matrix and finely distributed BaO (small dark
particles) (see Figures 8C and 8D). The crystallite
size of the $\gamma$-$Al_2O_3$ and barium containing phase was
30    about the same after calcination as that of bayerite
before calcination (see Figures 8B and 8D). After
calcination at 1000°C the autoclaved material
consisted of $\gamma$-$Al_2O_3$ which retained the shape of the
boehmite crystals (pseudomorphs) as shown in Figure
35    10B. The pseudomorphs were porous and the pore facets

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can be seen in Figure 10C.

The TEM images of microwaved material calcined for 1 hour at 1200°C, Figures 1 and 9B, show the start of the transition from $\theta$-$Al_2O_3$ to $\alpha$-$Al_2O_3$ in pure alumina and in alumina-baria samples, respectively. After calcination at 1400°C for 1 hour in air or argon, the microwaved material consisted of $BaAl_{13.2}O_{20.8}$ ($\beta_I$) particles of from 10 to 15 nm diameter and much larger $\alpha$-$Al_2O_3$ crystals as shown in Figures 9C to 9F. The $\beta_I$ particles were predominantly within the $\alpha$-$Al_2O_3$ crystals after calcination in air, but were distributed both within and on the surface of the $\alpha$-$Al_2O_3$ crystals after calcination in argon.

The autoclave treated material, calcined at 1400°C in air, consisted mainly of finely twinned $\theta$-$Al_2O_3$ with twin planes spaced about 5 nm apart as shown in Figures 11 A-D. The boehmite pseudomorph crystal shape was still retained although the internal porosity was much less than at 1000°C, and was more spherical in shape. The $\theta$-$Al_2O_3$ twin planes were parallel to the long axis of the pseudomorphs, i.e. the boehmite <001> direction. There was no evidence of sintering between the crystals and their size was similar to that at 1200°C. Small amounts $\alpha$-$Al_2O_3$ were observed. Detailed HRTEM examination of transition alumina structures in the autoclave treated samples indicated that the fine twinning in $\theta$-$Al_2O_3$ seen in the material calcined at 1400°C probably resulted from the ordering of cation vacancies in $\delta$-$Al_2O_3$ at lower temperatures. In contrast, autoclave treated material, calcined at 1400°C in argon, consisted of large crystals of $\alpha$-$Al_2O_3$ decorated on the surface with 10 nm particles of $BaAl_{12}O_{19}$ which has a

magnetoplumbite structure rather than a β type
structure (see Figures 12A and 12B).

5   The present invention provides a process whereby
transition alumina can be further stabilized against
thermal degradation to alpha-alumina. This results in
a catalyst which is effective at higher operating
temperatures and for longer times compared with the
prior art catalysts. An additional advantage of the
10  present invention is that it is very effective at
forming thin (approximately 1 to 5 μm) washcoats of
gamma-alumina on cordierite or other ceramic
substrates. This is important because the use in the
future of ceramic honeycomb substrates with a very
15  high channel density will require the use of thinner
washcoats. The process according to the present
invention can produce thinner films where (coated)
boehmite is used in the slurry, rather than gamma-
alumina.

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- 30 -

## Claims:

1.   A process for the production of a precursor
material for use in the preparation of a stabilized
alumina catalyst support material, which process
comprises the steps of:

(a)  providing a mixture comprising aluminium and
barium containing compounds; and

(b)  heating the mixture under conditions to form
particles of boehmite at least partially coated
with a layer comprising barium and/or a compound
of barium.

2.   A process as claimed in claim 1, wherein the
mixture comprising aluminium and barium containing
compounds is a substantially homogenous mixture.

3.   A process as claimed in claim 1 or claim 2,
wherein the layer formed on the particles of boehmite
comprises barium carbonate.

4.   A process as claimed in any one of the preceding
claims, wherein the aluminium containing compound
comprises aluminium chloride, aluminium nitrate,
aluminium sulphate, alumina and/or boehmite.

5.   A process as claimed in any one of the preceding
claims, wherein the barium containing compound
comprises barium chloride, barium sulphate and/or
barium nitrate.

6.   A process as claimed in any one of the preceding
claims, wherein the mixture comprising aluminium and

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barium containing compounds is in the form of a
substantially homogeneous precipitate.

7.   A process as claimed in claim 6, wherein the
substantially homogeneous precipitate is formed by a
process involving homogeneous precipitation of
aluminium and barium containing compounds from salt
solution.

8.   A process as claimed in claim 7, wherein the
homogeneous precipitation involves generating a base
within the salt solution through thermal decomposition
of a water-soluble reagent.

9.   A process as claimed in claim 8, wherein the
water-soluble reagent comprises urea and/or
hexamethylene tetramine.

10.  A process as claimed in any one of claims 7 to 9,
wherein the salt solution further includes a
dispersant, such as polyvinylpyrrolidone.

11.  A process as claimed in any one of claims 1 to 5,
wherein the mixture in step (a) is formed by adding a
solution comprising oxalic acid and a water soluble
barium compound, preferably barium nitrate, to an
aqueous slurry comprising boehmite.

12.  A process as claimed in any one of the preceding
claims, wherein heating of the mixture in step (b) is
achieved by a hydrothermal process.

13.  A process as claimed in claim 12, wherein the
hydrothermal treatment is carried out at a temperature
in the range of from 90 to 300°C, more preferably from

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100 to 220°C.

14.  A process as claimed in claim 12 or claim 13,
wherein the hydrothermal treatment is carried out at a
pressure in the range of from 1 to 150 bar, preferably
from 5 to 50 bar.

15.  A process as claimed in any one of claim 12 to
14, wherein the hydrothermal treatment is carried out
for a time in the range of from 30 minutes to 25
hours, preferably from 1 to 10 hours.

16.  A process as claimed in any one of claims 1 to
11, wherein the mixture in step (b) is heated at a
temperature in the range of from ambient temperature
to boiling temperature, preferably by a reflux
process.

17.  A process for the preparation of a stabilized
alumina catalyst support material, which process
comprises the steps of:

(i)   providing a precursor material comprising
      particles of boehmite at least partially coated
      with a layer comprising barium and/or a compound
      of barium; and

(ii)  heating the coated particles of boehmite to a
      temperature at which at least some of the
      boehmite transforms to gamma-alumina.

18.  A process as claimed in claim 17, comprising the
step of further heating whereby at least some of the
gamma-alumina transforms to theta and/or delta-
alumina.

19.   A process as claimed in claim 17 or claim 18, wherein said precursor material is produced according to a process as claimed in any one of claim 1 to 16.

5    20.   A process for the preparation of an automotive catalytic converter, which process comprises the steps of dispersing a mixture comprising particles of boehmite at least partially coated with a layer comprising barium and/or a compound of barium on a
10   metal or ceramic monolithic substrate, followed by heating the precursor mixture to a temperature at which at least some of the boehmite transforms to gamma-alumina.

15   21.   A process as claimed in claim 20, comprising the step of further heating whereby at least some of the gamma-alumina transforms to theta and/or delta-alumina.

20   22.   A process as claimed in claim 17 or claim 20, wherein heating is carried out at a temperature in the range of from 500 to 1000°C.

23.   A process as claimed in claim 18 or claim 21,
25   wherein the further heating is carried out at a temperature in the range of from 1000 to 1400°C.

24.   A process for the preparation of a catalyst, such as an automotive catalytic converter, which process
30   comprises the step of dispersing a stabilized alumina catalyst support material prepared according to the process of any one of claims 17 to 19 on a metal or ceramic monolithic substrate.

35   25.   A precursor material for use in the preparation

of catalyst support material, which precursor material
comprises particles of boehmite and/or transition
alumina at least partially coated with a layer
comprising barium and/or a compound of barium.

26. A precursor material as claimed in claim 25,
wherein the layer formed on the particles of boehmite
and/or transition alumina comprises barium carbonate,
barium oxide and/or barium aluminate.

27. A precursor material as claimed in claim 25 or
claim 26 provided in the form of a slurry or washcoat.

28. A stabilized alumina catalyst support material
which comprises gamma, theta and/or delta-alumina, and
which withstands substantial degradation to alpha-
alumina after exposure to a temperature of
approximately 1400°C for 1 hour.

29. A stabilized alumina catalyst support material as
claimed in claim 28, wherein particles of gamma, theta
and/or delta-alumina are at least partially coated
with a layer comprising barium carbonate, barium oxide
and/or barium aluminate.

30. A stabilized alumina catalyst carrier or support
material as claimed in claim 28 or claim 29 having a
specific surface area of at least 20 $m^2/g$ after
exposure to a temperature of 1400°C for 1 hour.

31. A stabilized alumina catalyst carrier or support
material as claimed in any one of claims 28 to 30
having a specific surface area of at least 31 $m^2/g$
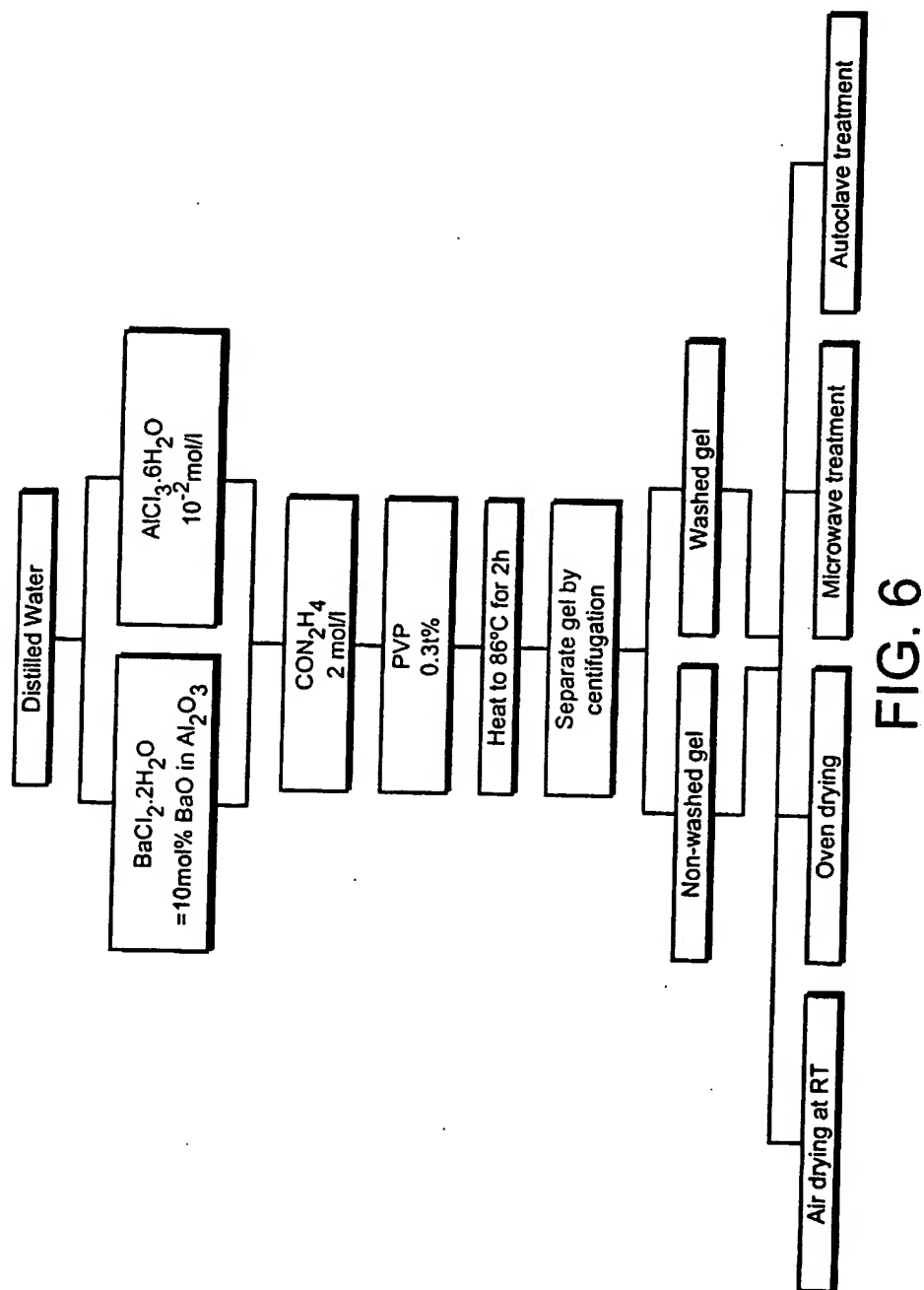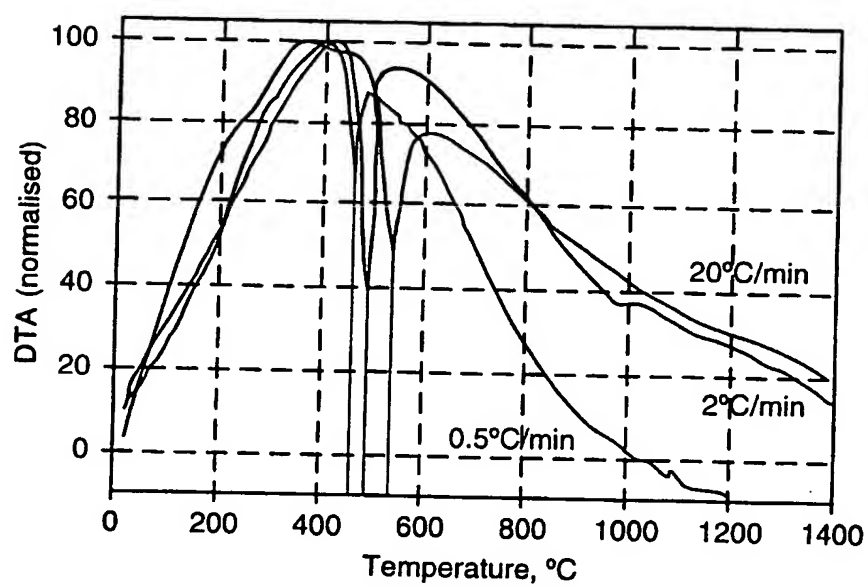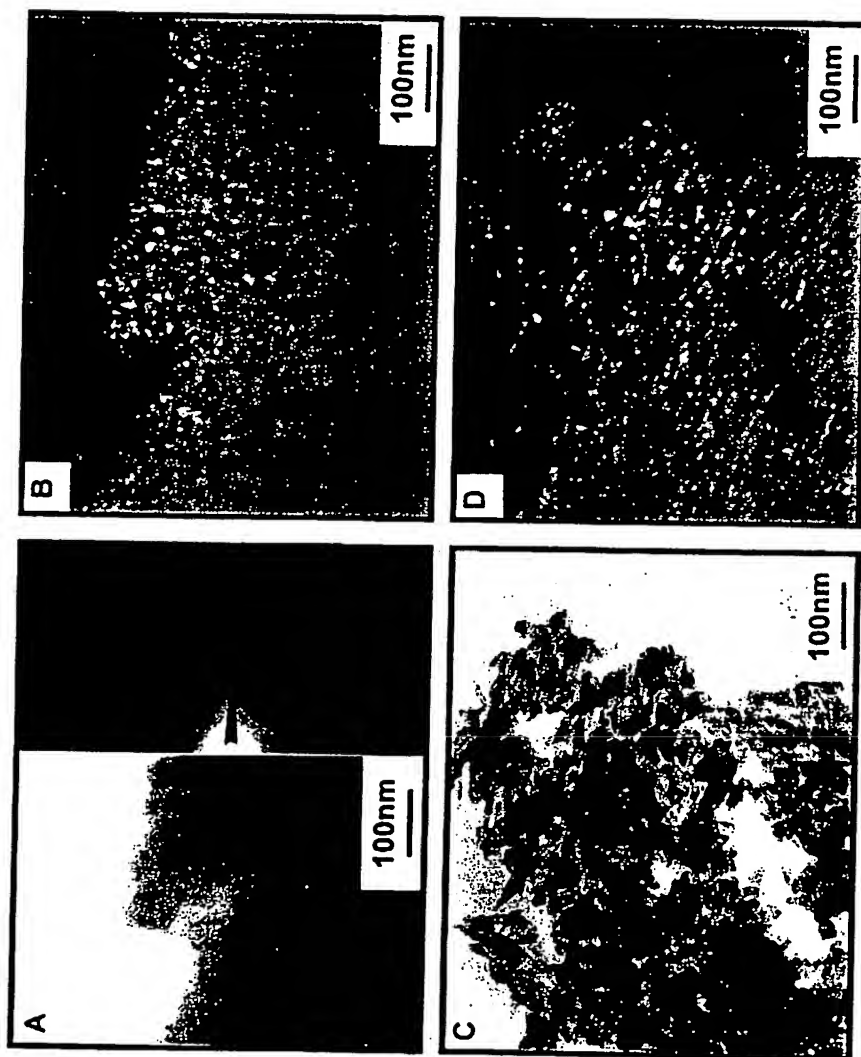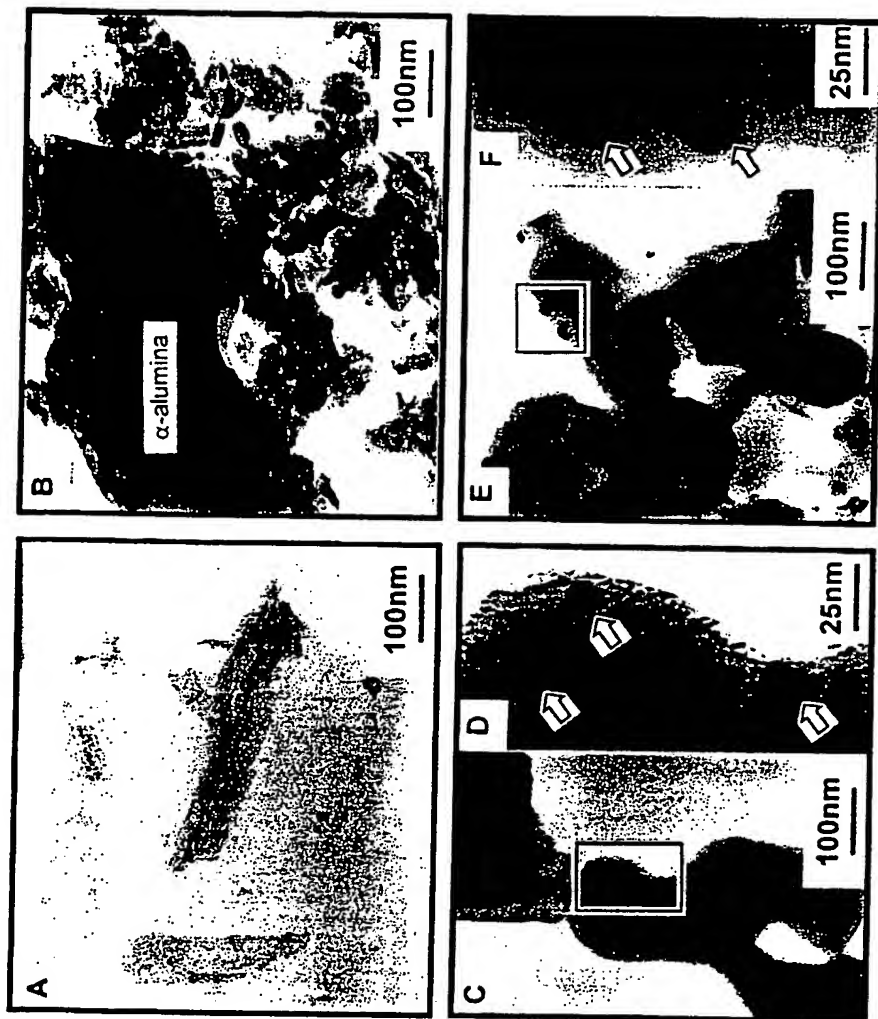after exposure to a temperature of 1400°C for 1 hour.

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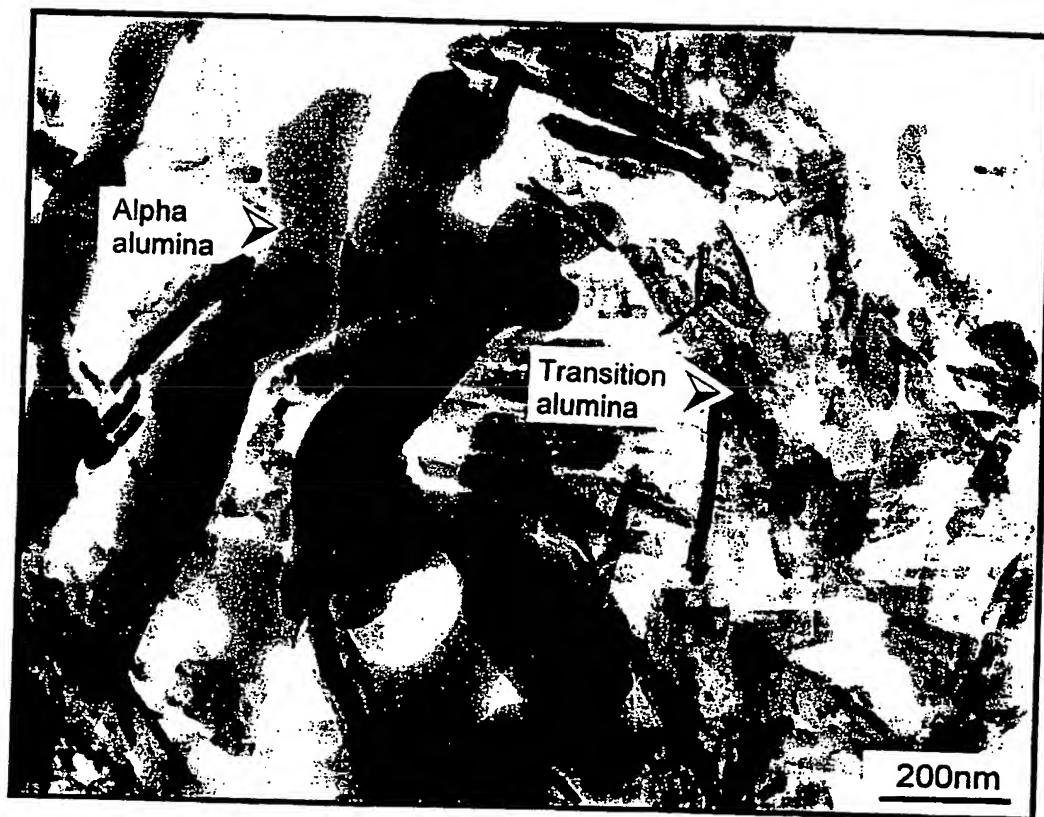

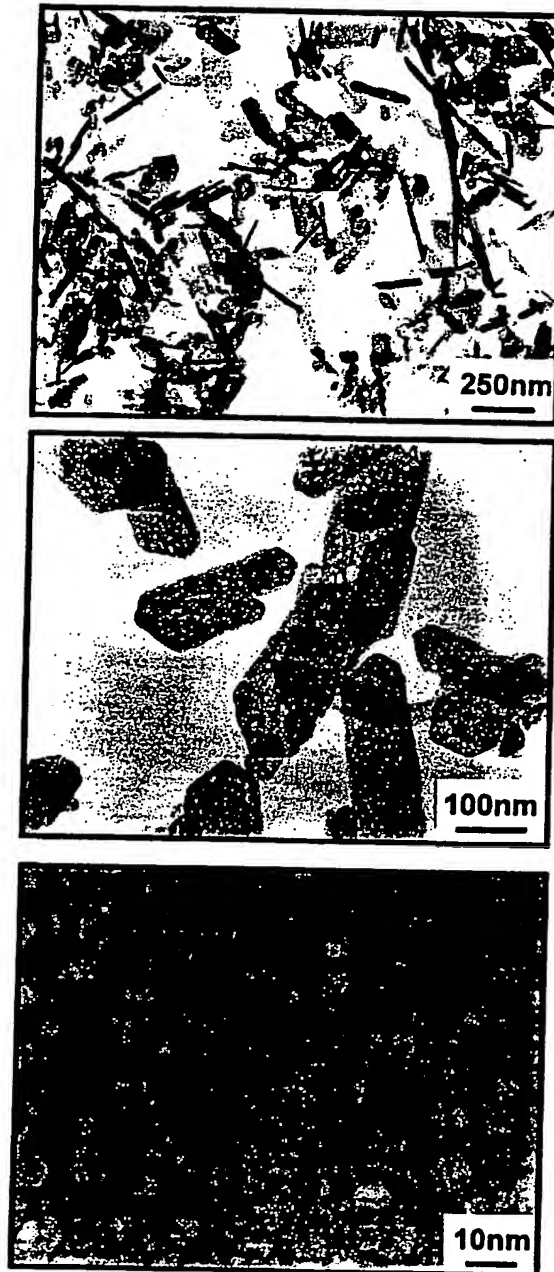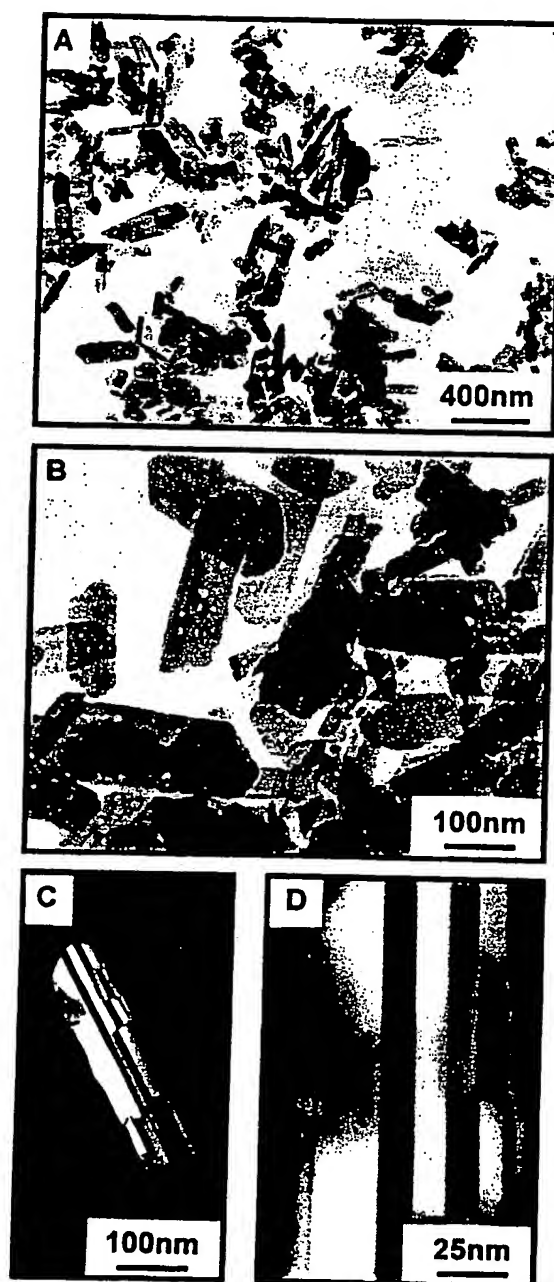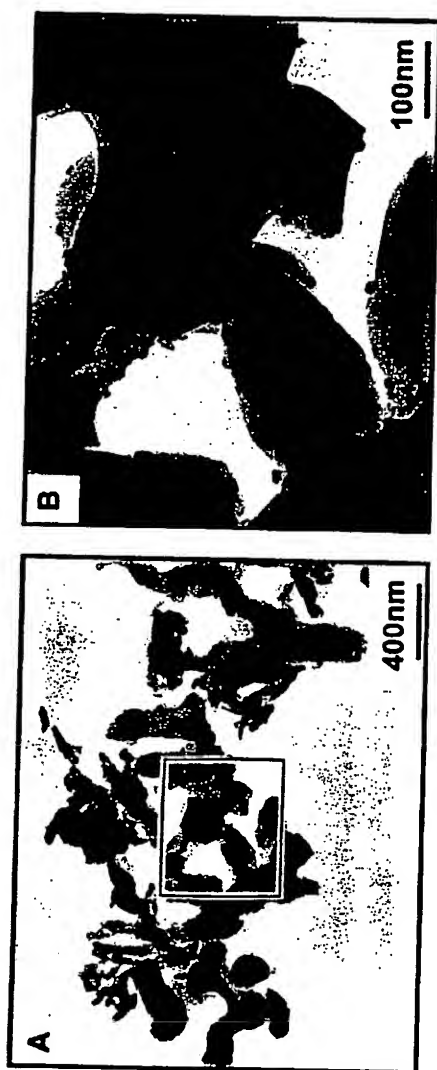
FIG. 1

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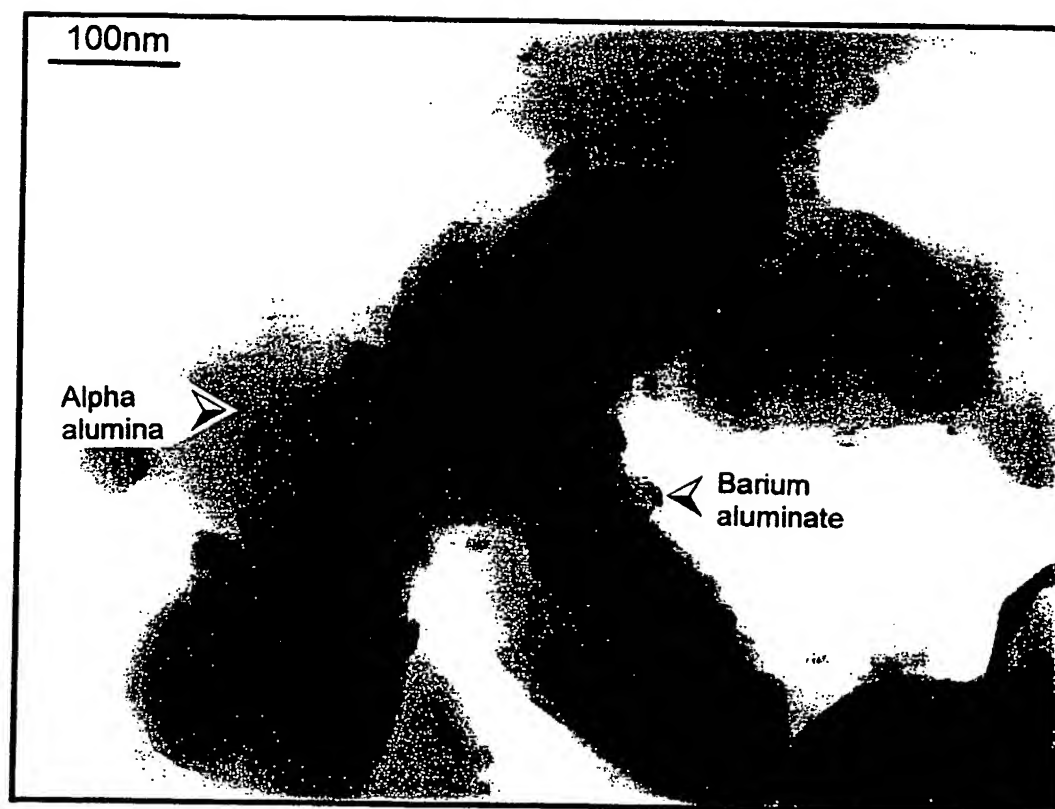


FIG. 2

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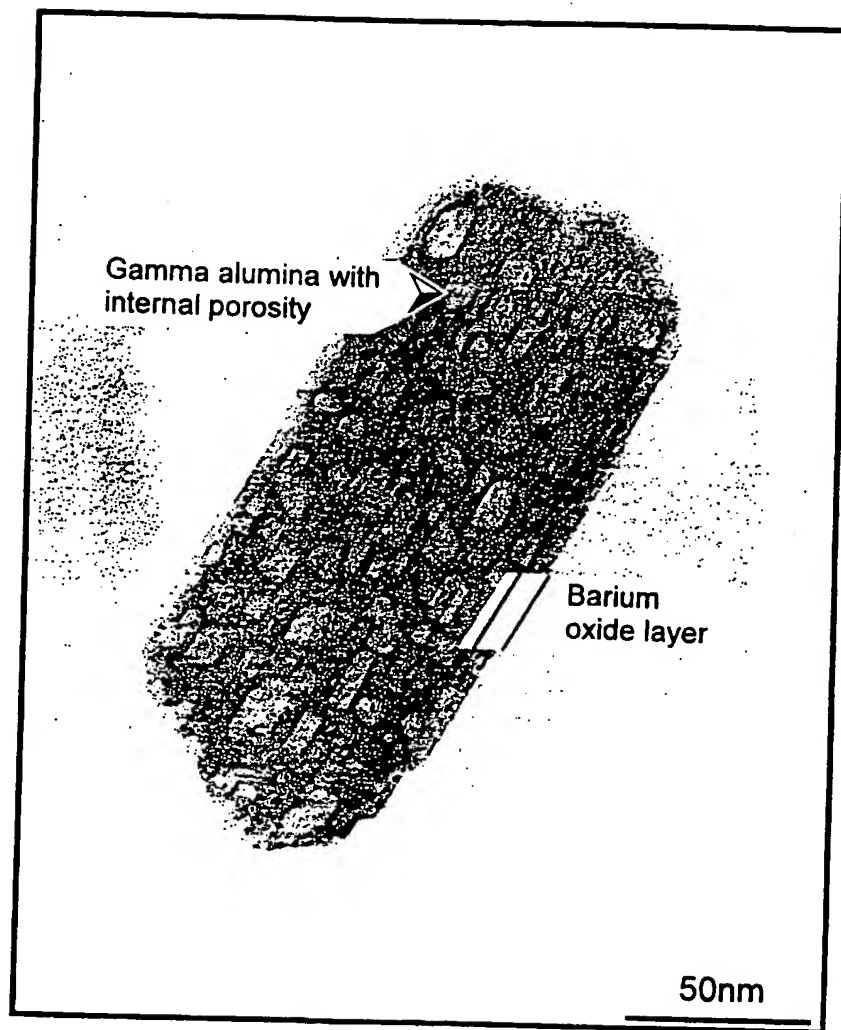


FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

FIG. 9

FIG. 10

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FIG. 11

FIG. 12

# INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 7     B01J23/02     B01J23/58     B01J37/02     B01D53/94

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 7     B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | DATABASE WPI<br>Section Ch, Week 199040<br>Derwent Publications Ltd., London, GB;<br>Class H06, AN 1990-302272<br>XP002140068<br>& JP 02 214541 A (TOYO KOGYO CO),<br>27 August 1990 (1990-08-27)<br>abstract | 1,2,17,<br>19,20,<br>24,27 |
| Y | ___ | 4-6 |
| Y | US 5 212 130 A (ADDIEGO WILLIAM P  ET AL)<br>18 May 1993 (1993-05-18)<br> claim 1 | 4-6 |
| A | ___<br>US 5 116 800 A (SUMMERS II JACK C  ET AL)<br>26 May 1992 (1992-05-26)<br>----- | |

☐ Further documents are listed in the continuation of box C.        ☒ Patent family members are listed in annex.

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 20 June 2000 | 28/06/2000 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,<br>Fax: (+31–70) 340–3016 | Thion, M |

| Patent document cited in search report | | Publication date | Patent family member(s) | | Publication date |
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| | | | DE | 69104062 T | 23-03-1995 |
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